

REMARKS/ARGUMENTS

Claim 1 has been amended to correct an obvious typographical error.

Claim 82 has been amended to eliminate confusion over which side of the metal webs is thicker since Example one indicates that the thicker (35  $\mu$ m) ID side faces the shell surface with the thinner (10  $\mu$ m) on side facing the tissue. The claim now merely requires one side to be thicker than the other.

In view of the above, each of the presently pending claims in this application is believed to be in immediate condition for allowance. Accordingly, the Examiner is respectfully requested to withdraw the outstanding rejection of the claims and to pass this application to issue.

If, however, for any reason the Examiner does not believe that such action can be taken at this time, it is respectfully requested that he/she telephone applicant's attorney at (908) 654-5000 in order to overcome any additional objections which he might have.

If there are any additional charges in connection with this requested amendment, the Examiner is authorized to charge Deposit Account No. 12-1095 therefor.

Dated: June 7, 2007

Respectfully submitted,

By 

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Preferably, the bonding between the metal webs and the metal particles is accomplished by sintering the metal particles to the webs. Also, preferably, the metal webs have partially hollow cores. The hollow cores of the metal webs may be surrounded by an outer web wall that has openings therein. The openings in the web walls are formed when the polyurethane foam material is pyrolyzed and turned into a gas which escapes through the web wall by forming an opening therein.

The pore size of the porous scaffold may range from 100  $\mu\text{m}$  to 1000  $\mu\text{m}$ . The pore volume may range from 50% to 90%. The scaffold may be formed into a shape having a thickness of 0.5 mm to 5 mm.

Preferably, the porous metal scaffold is bonded to a solid metal substrate. Also, preferably, the porous metal scaffold is directly bonded to the solid metal substrate. The metal scaffold may be sintered to the solid metal substrate. The scaffold may include a plurality of pores having a size greater than about 100  $\mu\text{m}$ . The metal particles may have a size of 20 to 100  $\mu\text{m}$  and preferably from 40  $\mu\text{m}$  to about 80  $\mu\text{m}$ . The metal of the particles is preferably selected from the group consisting of titanium, titanium alloy, cobalt chrome alloy, niobium and tantalum. The web metal is also preferably selected consisting of titanium, titanium alloy, cobalt chrome alloy, niobium and tantalum. The metal substrate may be part of an orthopedic implant.

The application of metal particles involves applying one or more layers of metallic powder and binding it to the pre-sintered metal foam structure by powder metallurgy techniques.

To control the pore size of the final foam the number of applications of the titanium powder is varied, which powder is

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# CHEMICAL VAPOR DEPOSITION (CVD)

Chemical vapor deposition (CVD) is a method of forming dense structural parts or coatings using the decomposition of relatively high vapor pressure gases. Gaseous compounds of the materials to be deposited are transported to a substrate surface where a thermal reaction/deposition occurs. Reaction byproducts are then exhausted out of the system.

CVD is a very versatile process used in the production of coatings, powders, fibers and monolithic parts. With CVD, it is possible to produce almost any metallic or non-metallic element, including carbon and silicon, as well as compounds such as carbides, nitrides, borides, oxides, intermetallics and many others. And applications are boundless.



A key advantage of the CVD process lies in the fact that the reactants used are gases, thereby taking advantage of the many characteristics of gases. One result is that CVD is not a line-of-sight process as are most other plating/coating processes. In addition to being able to penetrate porous bodies, blind holes, large L/D tubes, etc., CVD offers many advantages over other deposition processes. These include:

**Versatile – can deposit any element or compound**

**High Purity – typically 99.99-99.999%**

**High Density – nearly 100% of theoretical**

**Material Formation well below the melting point**

**Coatings Deposited by CVD are conformal and near net shape**

**Economical in production, since many parts can be coated at the same**

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# Refractory Ceramic Foams: A Novel New High Temperature Structure

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## INTRODUCTION

Advanced aerospace and commercial applications are challenging materials suppliers to develop low-density composites with improved high-temperature performance. In response to this demand, Ultramet has developed a process that adds a new category to the conventional carbon-carbon, metal-matrix, and ceramic-ceramic high-temperature materials.

These new materials are termed refractory foams. Ultramet's research reveals that useful, lightweight refractory bodies can be produced by the chemical vapor infiltration (CVI) of an extremely porous vitreous carbon body with a refractory material or combination of materials. The density of the resultant body is purposely maintained at less than full density, resulting in a structure with enhanced mechanical properties.

## FABRICATION

The use of cellular materials allows the simultaneous optimization of stiffness, strength, overall weight, thermal conductivity, surface area, and gas permeability. As such, these materials are highly desirable for a wide range of engineering applications. Cellular materials are the most efficient structure for many applications, and are the most common engineering material form in the natural world (e.g. wood and bone). Until recently, however, only wood was used to any great extent. Only during the twentieth century have man-made polymer foams been available for insulation, cushioning, padding, and packaging, but the high structural efficiency of cellular materials has been little used. A lack of engineering design familiarity with cellular materials, and a limited ability to tailor foams fabricated from engineering materials, have contributed to the lack of development of cellular structures.

Techniques now exist for fabricating foams not only of polymers, but of metals, ceramics, and glasses as well. These newer foams are increasingly being used structurally, for insulation, and in systems for absorbing the kinetic energy of impacts. Their uses exploit the unique combination of properties offered by cellular solids, properties that ultimately derive from the cellular structure of the material.

Several techniques are used to produce engineering (structural) foams. With the exception of

syntactic foams and self-foamed materials such as foam glass, these materials are produced using a foamed polymer as the starting material. From these economical precursors, three processing routes have been established for the production of ceramic and metallic foams. Ceramic foams can be produced by dipping the polymer foam in a slurry containing an appropriate binder and ceramic phases, followed by pressureless sintering at elevated temperatures. A second process used to make metallic foams utilizes an electroless process for the deposition of a metal onto the polymer foam precursor via electrolytic deposition.

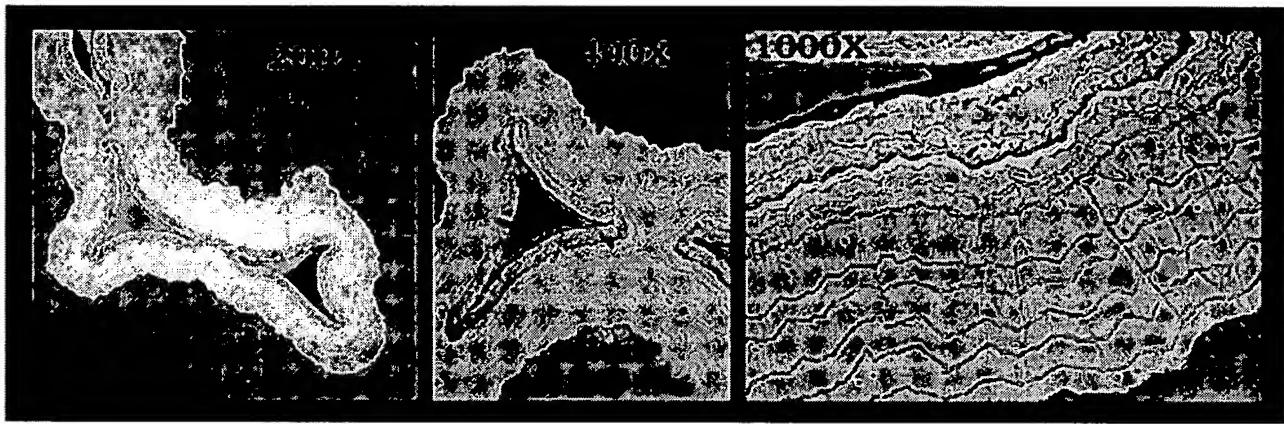
A third process, used exclusively at Ultramet, begins with the pyrolysis of the thermosetting polymer foam to obtain a carbonaceous foam skeleton. These carbonaceous foam materials are themselves attractive for many aerospace and industrial applications, including thermal insulation, impact absorption, catalyst support, and metal and gas filtration. They are thermally stable, low in weight and density, and are chemically pure; they have low thermal expansion, resist thermal stress and shock, and are relatively inexpensive. These Ultrafoam<sup>®</sup> materials are becoming readily available, can be furnished in various sizes and configurations, and are easy to machine, maintain and repair.

### FOAM CELL STRUCTURE



Ultramet takes this process several steps farther by infiltrating the vitreous carbon Ultrafoam skeleton with refractory material(s) using CVD/CVI. In this process, 10-1000 microns of the desired refractory metal or ceramic are deposited onto the interior surfaces of the reticulated carbon foam. The structural integrity of the resultant refractory foam composite material (Ultrametal<sup>®</sup>) is greatly enhanced by the deposit, and the properties of the composite are dominated by the structure and properties of the deposit. The mechanical properties for a given material and density are often one to two orders of magnitude higher compared to slurry-cast materials because the CVD deposit is typically 100% dense with grain sizes less than 1-5 microns (although larger or smaller grains can be deposited) and <0.05% impurities.

The Ultramet process utilizes the high deposition rates of CVD (100-400  $\mu\text{m/hr}$ ) while depositing material within the foam structure via a combination of CVD and CVI techniques. The open-pore carbon foam precursor is heated to the temperature suitable for the desired deposition reaction, while the reactant gases are pulled through it. The gaseous precursor compound is reduced or decomposed at the foam surfaces, forming a uniform nanolayered deposit throughout the internal structure of the foam, with the nanolayering adding enhanced mechanical properties. The carbon lattice functions only as a substrate for the material being deposited.



It is important to note that the structural integrity of the fabricated foam composite is provided by the deposited thin films, rather than the carbon substrate. These films have much higher elastic moduli than the thin sections of vitreous carbon in the foam. Their high stiffness relative to the carbon results in their supporting the mechanical load for the entire body, ensuring that failure does not occur in the carbon. Because of the superior properties of the deposited films, the individual ligaments act as microcellular materials, with 70-100% of the strength being contributed by the deposit.

Refractory foams can be fabricated from any material or materials combination (either simultaneously deposited or layered) which can be deposited by CVD/CVI. Among the materials that can be deposited are the refractory metals (e.g. zirconium, niobium, hafnium, tantalum, tungsten, rhenum) and their ceramic compounds (e.g. the oxides, nitrides, carbides, borides, and silicides). Deposited material densities of up to 50% of theoretical values can be readily achieved. Stiffness, strength, thermal conductivity, and overall weight may be simultaneously optimized for a given application by varying the chosen deposited materials and their densities.

Structural applications often benefit from the low density, low thermal conductivity, and excellent thermal shock resistance of the foam composite, but require greater mechanical properties (flexural, tensile) than the basic Ultramet can provide. Flexural and tensile properties can be greatly enhanced if an adherent, continuous sheet is applied to the surfaces of the foam. Face sheets have been applied directly via CVD by changing process conditions and gas flow patterns to promote surface deposition, as well as by diffusion bonding, brazing, mechanical fasteners, and adhesives. The specific attachment method is determined by use conditions (e.g. temperature, stress, strain, environment, weight requirements) and can be optimized for strength, weight, adhesion, environmental resistance, etc. The applied face sheet (s) can be the same material as the foam, a totally different material, or a combination of both, as conditions require.

## MECHANICAL PROPERTIES

The elastic properties at small deformation in foams can be calculated from the linear elastic bending of a beam of length  $l$  loaded at its midpoint for a regular square area of cells. In this manner, the relative density can be related to the Young's modulus, shear modulus, and Poisson's ratio respectively:

$$E^* = \frac{\sigma}{\epsilon} = \frac{C_1 E_s I}{l^4} \approx E_s \left( \frac{\rho^*}{\rho_s} \right)^2 \quad (1)$$

$$G^* = \frac{\tau}{\gamma} = \frac{C_2 E_s F}{l^4} \approx \frac{3}{8} E_s \left( \frac{\rho^*}{\rho_s} \right)^2 \quad (2)$$

$$\nu = \frac{C_1}{2 C_2} \approx \frac{1}{3} \quad (3)$$

This analysis necessarily includes a number of approximations; for example, the way in which density is calculated double counts as the cell vertices, and the axial and shear displacements of the cell walls have been neglected.

A similar model results in equations for the elastic collapse strength, plastic collapse strength, and brittle fracture strength of foam materials. These relationships can be expressed as follows:

$$\text{For elastic collapse: } \sigma_{el}^* = .05 E_s \left( \frac{\rho^*}{\rho_s} \right)^2$$

$$\text{For plastic collapse in early stages: } \sigma_{pl}^* = .30 \sigma_{ys} \left( \frac{\rho^*}{\rho_s} \right)^{3/2}$$

$$\text{For plastic collapse, maximum tension: } \sigma_{pl_{max}}^* = \sigma_{ys} \left( \frac{\rho^*}{\rho_s} \right)$$

$$\text{For brittle crush strength: } \sigma_{cr}^* = .65 \sigma_{ts} \left( \frac{\rho^*}{\rho_s} \right)^{3/2}$$

$$\text{For fracture toughness (brittle fracture): } \frac{K_{Ic}}{\sigma_{ts} \sqrt{A}} = .65 \left( \frac{\rho^*}{\rho_s} \right)^{3/2}$$

Precise and accurate control over the physical properties of the resultant foam is easily attained, and may be optimized for a given application by varying the infiltration times in order to control the final density. An even greater degree of control may be attained by manipulating the pore size and shape of the cell geometry. By manipulating cell geometry in the carbon skeleton, properties may be optimized with respect to direction, the Poisson's ratio may be varied from -0.7 to 0.4, and the fracture toughness and impact resistance may be increased

over those of basic isotropic foams. Although modeling work is still required to account for the effect of varied cell geometry, the ability to manipulate geometry is extremely advantageous when producing sandwich components

## APPLICATIONS

One application of this technology is in the fabrication of thermal insulation material. Preliminary measurements of zirconia refractory foam reveal that thermal insulation equivalent to that of the NASA space shuttle protective thermal tiles can be achieved at a 1000°F higher operating temperature. Using innovative techniques, Ultramet has fabricated insulation with a density gradient through the cross section of the material. This procedure makes it possible to blend a high-density surface with good mechanical properties into a region with low thermal conductivity. Other unique thermal structures may be created by depositing a structural material, such as niobium, on one portion of the cross-section and an insulator, such as zirconia or hafnia, on the opposite side.

Another potential application using this technology involves overcoating rhenium or niobium foam with iridium or platinum for lightweight, high-temperature oxidation-resistant structures. Ultramet also has produced boron carbide and silicon carbide foam structures that possess extremely high stiffness-to-weight characteristics. And using a SiC foam core composite panel, Ultramet has demonstrated a 60-80% weight savings over conventional carbon/phenolic and carbon/carbon heat shields for reentry protection. Additional stiffness-driven applications currently under study include lightweight nozzle flaps for advanced turbine engines and aerobraking structures, and aircraft wind and fuselage structures.

Applied to high temperature filtration problems these foam materials have seen service in air bags, solid rockets, and molten metal filtration. With the addition of a catalytic coating these foam materials serve as pollution control devices for unburned hydrocarbons and catalytic ignitors for rocket engines. In addition, when coated with a biocompatible material such as niobium or tantalum, these foam materials can be used for structural in-body implants to promote bone and tissue growth and also used for ex vivo three dimensional cell growth.

## CONCLUSIONS

The flexibility of CVD permits the fabrication of a large number of materials in various geometric forms, one of which is the porous cellular structure. The fabrication of such a structure begins with the pyrolysis of a resin-impregnated thermosetting foam to obtain a reticulated carbon foam skeleton. The foam ligaments can then be coated with a variety of materials (metals, oxides, nitrides, carbides, borides, silicides, etc.), either singly or as hybrid, layered, alloyed, or graded structures. During this process, 10 to 1000 microns of the desired material(s) are deposited onto the foam ligaments by a CVI a variation of CVD. The thermomechanical properties of the resultant structure are dominated by the properties of the deposit, becoming independent of the carbon properties at very small material loadings. With precise control over the variables available, it is possible to obtain the simultaneous optimization of stiffness, strength, thermal conductivity, overall weight, and environmental resistance.



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